MEASURING POTENTIAL ABSORPTION AND RESIDUE PENETRATION OF LEATHER OR VINYL GLOVES USED DURING HARVEST IN ROSES

By

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HS-1537 January 16, 1990

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SUMMARY

The use of leather and sewn-vinyl gloves by the field-grown rose industry for protection from physical trauma has raised concerns of their suitability as chemical resistant hand protection when working with propargite-treated plants. These glove materials are employed because of their high abrasion/puncture resistance, properties that traditional chemical resistant plastic or rubber gloves often lack. Under conditions of both actual use exposure and controlled laboratory exposure, propargite, as formulated in OMITE^{R} 30W, was non-extractable from both the leather and vinyl gloves. This apparent binding of the propargite may also make it unavailable for biological activity (dermal absorption). The exact mechanism of non-extractability is unknown, but this suggests that leather/vinyl gloves may provide adequate protection from propargite plant residue. No measures of propargite levels in the field were possible since the foliage had been removed, but propargite was not found on either dosimeter gloves or work gloves. Under conditions of this harvest, worker hand exposure to propargite was below detectable levels.

Objective

The use of gloves for the mitigation of hand exposure to pesticides is a common practice in agriculture. In most cases, chemical-resistant gloves are the accepted method to prevent dermal exposure to pesticide concentrates and residues. Disposable cotton gloves have been under consideration by CDFA for use by harvesters in grapes and are used by harvesters in many row crops. However, a special case for hand protection is found in the rose production industry. Not only is there a need for protection from pesticide residues, but there is also a requirement for protection from the physical trauma associated with rose thorns. This puncture-resistance requirement is, in fact, of equal importance to the chemical resistance properties of the glove. The material most often used is leather, followed by a rubberized canvas. Also used by the rose growers in their sorting operations is a vinyl-cloth glove. The use of leather has raised some questions about the degree of chemical protection afforded by leather and if the leather may actually lead to a chronic exposure by acting as a resevoir for continued exposure after the environmental source is removed. The U.S. Environmental Protection Agency has promolgated proposed rules concerning leather gloves (**Fed. Reg.** Vol. 53, No. 131, pg. 25985, para. c, Friday, July 8, 1988) and has considered leather and cloth gloves unacceptable, without adequate justification. This study investigated two potential exposure conditions: one day penetration of material through new gloves and penetration over extended use.

Additionally, absorption/adsorption of pesticide residue to both the leather and vinyl gloves was investigated. The pesticide of greatest use in the rose industry of Kern County is propargite (OMITE^{R} 30W). This material was used as an indicator/model for pesticide residue exposure. Additionally, propargite has come under consideration for further regulatory control because of adverse reproductive effects in rats. This study allowed not only for general pesticide exposure assessment, but also for specific assessment of propargite exposure.

Product Information

PESTICIDE: **Propargite** 2-{4-(1,1-dimethylethyl) phenoxy}cyclohexyl 2-propynyl sulfite
FORMULATION: OMITE 30W (wettable powder)
EPA REG. NO.: 400-82 AA
TARGET CROP: Roses, field grown

Methods & Materials

To validate the chemical analysis method used to remove and quantitate propargite from both the leather, vinyl and cotton matrices, ten pair of gloves were obtained from the grower. Five pair were new, unused gloves (three leather and two vinyl) and the other five pair were used gloves taken from workers handling rose plants. Half of the gloves (right-hand) were analyzed without further processing; the other half (left-glove) were spiked with different levels of OMITE^{R} 30W. The age of the gloves was unknown but not more than 30 days, according to the foreman. These gloves were shipped to the California Department of Food and Agriculture's Chemistry Laboratory Services (CLS) in Sacramento, for use in spiking studies (adding known amounts of propargite to gloves for validating propargite extraction method

from gloves) and controls (unused, uncontaminated gloves). The protocol for the spiking procedure is listed in APPENDIX I.

The first phase of the study was concerned with the one-day penetration of propargite through the gloves during rose-handling operations associated with harvest. Two operations were monitored: harvesting and sorting bare-root stock plants. Harvesting involved removing the leaves from the plants (mechanical method/no worker contact), uprooting the plant (mechanical method/no worker contact), gathering the plants into bundles (worker contact with the stems), tying the bundles (worker contact with roots and stems), and tossing the bundles onto a flat-bed field-trailer (contact with stems, roots and soil). Harvesters wear, as a minimum, leather gloves, long-sleeved shirts, long-legged pants and shoes/boots. Since the season of harvest is winter, and cool temperatures are normal (32° to 50°F), the workers often wore coats, extra shirts and other body covering just to keep warm. The work task that the monitored harvesters were primarily engaged in was tying. When necessary, they also assisted in gathering.

Sorting was done in a large shed. The bundled plants were brought into the shed and removed from the trailers. The bundles were untied and the stems separated. The stems were transported via conveyer belt to sorters who sized and graded the plants, handling the plants as they did so. These workers also had multiple layers of clothing, often starting with street clothes covered with coats/jackets covered with aprons/rainsuits covered with sheets of plastic. The primary purpose of this clothing was also thermal protection, but additionally for moisture protection from the damp plants. At least one pair of gloves was worn, and sometimes more. All workers were required to wear safety glasses. The sorting shed was also a very cool environment and the foreman said that it is doubtful any less clothing would be worn at this job-site.

Five workers were selected from the sorting crew and 10 from the harvesters for a total of 15 workers participating in the study. The workers were code identified as to name and work activity. All sorters were female and all harvesters were male. All workers were right-hand dominant. The harvesters were issued one pair of light-duty 100 percent cotton gloves to be used as internal (protected) dermal dosimeters. Due to the tight fit of their gloves, sorters were not issued the internal dosimeters. The workers were also issued the appropriate glove for their work activity: leather for harvest and vinyl for sorting. Workers were instructed to use the gloves as they would throughout the work day and to avoid removing the gloves while in potential contact with contaminated material. An ergometric analysis of the work activities was performed for each of the work sites (see APPENDIX II).

At the end of the first work period, the gloves and dosimeters were collected. Each glove was stored separately in its own container: cotton gloves were placed into 4 oz. glass wide-mouth jars, sealed with aluminum foil and capped with plastic lids; exterior gloves were placed into plastic bags (GLAD Brand ZIPLOC^{R} plastic bag, 1 gallon size) and sealed flat in the bag. Each glove was identified as to worker code. The dosimeters and gloves were stored in FREEZE SAFES^{R} loaded with dry ice to maintain an approximate temperature of -70°C. Post-exposure cross-contamination between the interior and the exterior of the leather and vinyl gloves was avoided by making sure the gloves were stored undistorted (not inside out) and pressed

together. The samples were shipped to CLS for analysis. Results were reported as total propargite recovered per item.

The second phase of the study started immediately as the first phase was ending. As the workers returned the gloves of the first phase, they were issued a second pair of gloves like the ones they returned; leather for harvesters, vinyl for sorters. These gloves were marked to code identify the worker. The workers were instructed to use these gloves for one week in the manner they normally use gloves assigned to them by their employer.

The gloves which the harvesters were issued in the second phase turned out to be inadequate (too thin) for the assigned work tasks. Within two to three days the leather gloves were rendered useless because of excess abrasive wear and the workers returned the gloves to their foreman. The expected life of leather gloves used in harvest is between five days to two weeks, depending on the amount of contact with the rose plants. The gloves were collected by the cooperator, bagged in the appropriate plastic bags and stored in a cool (~45°F) environment. The harvesters were reissued new, heavier-duty (thicker) leather gloves and continued their work. The sorters did not have any problems with their gloves. However, from time to time, especially during wet weather, the sorters may also have covered these gloves with waterproof overgloves. No full documentation is available, but during the time they were under observation, they did not wear overgloves. The wearing of overgloves is an optional cultural practice but was not observed in the monitored workers.

Following one week of use, at the beginning of the work day, each harvester was again asked to don a pair of cotton hand dosimeters under their exterior gloves. At the end of the work day the cotton dosimeters were collected and the workers were asked to continue using the same outer gloves. They were also asked not to discard the leather gloves when they failed, but to return them to their supervisor, who would store them for later analysis. The prematurely failed gloves, which had originally been distributed at the beginning of the second phase, were collected for anaylsis. The sorting crews continued to use their vinyl gloves. Collected gloves were stored and analyzed in the same manner as cited earlier.

Another seven days of work were performed by the crews. At the end of this period, the harvesters again wore the dosimeter gloves under their leather gloves. On many of these gloves the structural integrity had been compromised. In fact, all the harvesters would cut a slit in the ring-finger of each glove to allow a cutting-hook worn on that finger to project through the glove. The cutting-hook was used to cut the twine after bundling the roses. Other points of failure were on the fingers' dorsal side and in the palmar region. However, these are conditions normal to the agricultural practices associated with rose harvest.

At the end of the work period, the dosimeter gloves and the exterior gloves of both the harvesters and sorters were collected. Storage and analysis were the same as before.

The CLS method for OMITE^{R} 30W analysis from gloves is given in APPENDIX III.

Results

The spiked-glove extracts were uniformly negative for propargite. Even after addition of 30 mg of material to the gloves, none of the gloves showed detectable levels of residue following extraction with ethyl acetate. It would appear that formulated product is strongly bound in some way to the glove matrices and is unavailable for analysis. The binding may be to the glove material or may be "stuck" in the pores of the leather or chemically bound to the vinyl. The mechanism of binding is currently unclear. However, this presumably also means it is unavailable for biological absorption. During processing of the formulated product for spiking, the insoluble carrier materials were filtered out. On confirmatory analysis, the filtrate used for spiking had propargite present. Therefore, the propargite was not being filtered out with the insoluble materials. The lack of residue on the gauze, which was inserted inside the spiked gloves to intercept any penetrated residues, also suggests that the gloves were affording some kind of barrier protection. The gauze was in close contact with the palm of the glove and should have picked up glove-penetrating residues. But gauze extracts were also negative (MDL = 20 ug/extract). Table One shows the results of the laboratory spike analysis.

When it became clear that the lab-spikes were giving unusual results, only a subset of the glove samples were analyzed. In light of the findings of these laboratory spikes, it is not suprising that the representative number of experimental gloves analyzed also had non-detectable levels of residue. Used gloves showed no detectable levels (MDL = 100 ug/extract). It is safe to assume that the workers probably did not wear the leather gloves at all times and that some contamination from exterior sources would be inevitable. Nonetheless, nothing detectable was found on this matrix either. Table Two gives the results of the analysis of the experimentally used gloves.

Discussion & Conclusions

The data suggest that the potential for rose-harvester and rose-sorter exposure to propargite is negligible. No detectable propargite was found on any of the test matrices nor on any of the spike-recovery samples. The interpetation of the former results could be that either there was no propargite in the field (full degradation had occurred) or that the gloves were providing some kind of protective factor. It is known that propargite had been applied to the field about 90 days prior to harvest. Although foliage samples were not part of the sampling protocol, no leaf samples could have been collected since the plants were mechanically de-leafed before harvester contact. The stem and root structure are the sole parts of the plant that workers may contact. It is reasonable to assume that hand exposure to propargite for harvesters and sorters, under the conditions of this study, is negligible.

The results from the laboratory work are quite interesting and bear further consideration. Chemistry Laboratory Services made every attempt to extract the propargite (from OMITE^{R} 30W) that they had added to the gloves. Different solvents were utilized in an attempt to extract the propargite from the gloves, but the results were uniformly negative. The spiking solution was tested when the unusual results began to occur; the appropriate amount of propargite was found in all the spiking solutions. Some type of "binding" had made the propargite (from OMITE^{R} 30W) unavailable for chemical

analysis. Recovery was achieved when analytical standards were used rather that propargite from OMITE^{R} 30W. The mechanism of OMITE^{R} 30W binding is unknown, as is the role played by the "inert ingredients" in this binding process. Since a known amount of propargite was added to the test gloves, it is reasonable to believe that the material was on the gloves when they were analyzed. Another analysis using radiolabeled OMITE^{R} may be required to answer the questions raised by this study. The only information available from this study is that OMITE^{R} 30W is not extractable on either leather or vinyl gloves of the type tested, even when milligram amounts of the material were added to the glove. The bioavailibility of the OMITE^{R} 30W can only be assumed to parallel its extractability.

TABLE ONE
SPIKES FOR LEATHER/VINYL/GAUZE

All leather gloves and associated gauze had non-detectable levels of propargite when analyzed. The column "MDL" refers to the minimum detectable level on that media.

Media ID	Matrix Leather	MDL (ug)	Matrix Vinyl	MDL (ug)
USED/Unspiked	CON 1*	100	CON 4	40
	CON 2	100	CON 5	40
	CON 3	100		
USED/Spiked	**100 ug[x]**	**100**	**10 ug**	**40**
	1,000 ug	**100**	**10,000 ug**	**40**
	10,000 ug	**100**		
UNUSED/Unspiked	UNU 1+	100	UNU 4	40
	UNU 2	100	UNU 5	40
	UNU 3	100		
UNUSED/Spiked	**300 ug**	**100**	**30 ug**	**100**
	3,000 ug	**100**	**30,000 ug**	**100**
	30,000 ug	**100**		
Gauze used in	300 ug	20	30 ug	20
UNUSED/Spiked	3,000 ug	20	30,000 ug	20
	30,000 ug	20		

* CON refers to contaminated (used) glove matrix
\+ UNU refers to uncontaminated (unused) glove matrix
x value refers to amount of propargite used as spike

TABLE TWO
ANALYTICAL TEST RESULTS

MATRIX TYPE	DAYS OF EXPOSURE/USE	RESULTS/MDL
Cotton	0	ND/20 ug
Cotton	0	ND/20 ug
Cotton	1	ND/20 ug
Cotton	3	ND/20 ug
Leather	1	ND/100 ug
Leather	1	ND/100 ug
Leather	5	ND/100 ug
Vinyl	1	ND/40 ug
Vinyl	14	ND/40 ug

Appendix I

DIRECTIONS FOR PREPARATION AND ANALYSIS OF GLOVE SPIKE SAMPLES

For the used gloves marked CON-1L through CON-5L, treat the glove as a normal sample extraction for propargite analysis. For gloves marked CON-1R through CON-5R, use the following spiking scheme, using 2 ml of water as the solvent:

USED GLOVES

CON-1: Add 100 ug propargite
CON-2: Add 1,000 ug propargite
CON-3: Add 10,000 ug propargite
CON-4: Add 10 ug propargite
CON-5: Add 10,000 ug propargite

Place the solution in the center of the palm of the gloves. Allow gloves to dry overnight at ambient temperature.

For unused (new) gloves marked UNU-1L through UNU-5L, treat the gloves as knormal blank sample extractions for propargite analysis. For gloves marked UNU-1R through UNU-5R, place a 57.76 cm^2 gauze pad inside the glove, centered at the palm. Lay the glove palm-up on the workbench. Using the same treatment rates as the CON series, add propargite to the glove, but repeat the additions 2 more time, 24 hours apart, for a total of 3 treatments in 3 days. Total added propargite will be:

NEW GLOVES

UNU-1	300 ug
UNU-2	3,000 ug
UNU-3	30,000 ug
UNU-4	30 ug
UNU-5	30,000 ug

The gauze pads will remain in place during all three days of treatment and will be removed and analyzed for propargite at the end of the third day. The source of propargite will be formulated product; OMITE^R 30W. The amount of propargite refers to active ingredient and not formulated product weight.

Appendix II

ERGOMETRIC ANAYLSIS OF WORK TASKS PERFORMED DURING ROSE HARVEST AND SORTING

Harvest

1. Tractor drives along rows pulling the plant up-rooting unit. Up-rooter, using a large subterrainian blade, undercuts the rose bush roots then deposits the bush behind as the tractor advances.

2. Stackers come along up-rooted plants and begin to stack them in batches of 5 to 10, shaking off excess soil. All plants are layed along the same orientation in each batch.

3. Bundler/tiers wrap each batch into bundles using twine loops around the batches, looping around the plants then compressing the bundle with their feet while tying off the bundle and cutting the twine. These were the workers who were monitored in this study.

4. Collecters then take bundles and place (toss) them into flatbed trailers for removal to the sorting facility.

Though these are discrete functions normally performed by different persons, it is not unusual for all three gathering functions (stack-bundle-collect) to be done by all harvesters, depending on the back-up of the various tasks' workloads.

Sorter

1. Rose bundles are off-loaded from flatbed trailers onto conveyer belts. Sometimes these trailers are left beneath water sprinklers to maintain a moist environment for the plants.

2. Rose bundles have their twine restraints removed and the plants are layed out singly onto a perpendicular running conveyer belt.

3. Sorters inspect each plant for size, grade and other surface defects. This involves picking up each plant as it goes by, visually assessing the plant, rejecting culls onto a different conveyer, and re-placing the first-quality plants back onto the conveyer. These were the workers who were monitored in this portion of the study.

4. Inspected plants continue into the processing channels.

The sorters, unlike the harvesters, do not appear to move out of their own job tasks.

Appendix III

Analysis of OMITE 30W from Gloves

Billy Fong, Agricultural Chemist II

SCOPE: This procedure is suitable for the analysis of various gloves: leather, vinyl and cotton.

PRINCIPLE: Gloves are extracted in glass jars with ethyl acetate by sonication. Extracts are analyzed by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Ethyl acetate, pesticide grade
2. 100 ml cap. glass jars for cotton gloves
3. 2 qt. MASON jars for vinyl gloves
4. 1 gal. glass jars for leather gloves
5. GC equiped with sulphur-specific detection or electron capture detector

ANALYSIS: Insert glove pairs into appropriate glass containers. Cotton gloves can be rolled up in order to fit, whereas vinyl and leather should not. Add 100 ml ethyl acetate to cotton gloves, 200 ml to vinyl and 500 ml to leather. Place all jars in sonicator for 45 minutes. Extracts may be concentrated prior to analysis provided no interferences exist.

EQUIPMENT CONDITIONS:

Varian 3700 GLC with Electron Capture Detector (ECD)
Column: packed, 6 ft. 2% SP2100
Column Conditions: 240°C, He gas @ 30 psi
Injector Conditions: 250°C
Detector Conditions: 260°C
Attenuation X Range: $64 \cdot 10^{-11}$

Varian 6000 GLC with Hall Electroconductivity Detector
Column: megabore, 0.5 mm X 10 m HP-17
(50:50 phenylmethyl:methyl silicone)
Column Conditions: 210°C, He gas @ 15 psi
Injector Conditions: 220°C
Detector Conditions: 250°C
Attenuation X Range: 5 X 1
Vent: 0.5 min.

Varian 6000 GLC with Flame Photometric / Sulphur Mode
Column: megabore, 0.5mm X 10m HP-1
(methyl silicone)
Column Conditions: 240°C, He gas @ 5 psi
Injector Conditions: 250°C
Detector Conditions: 260°C
Attenuation X Range: $1 \cdot 10^{-11}$

$$\text{Total ug} = \frac{\text{(Peak Height Sample)(ng STD)(ml Final Volume)}}{\text{(Peak Height)(ul Injection)}}$$